

PATENT ABSTRACTS OF JAPAN

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(54) LIQUID AGENT FOR IMPROVING SURFACE QUALITY OF PAPER

(57)Abstract:

PURPOSE: To improve the surface strength, internal bond strength and sizing effect of paper in balanced state.

CONSTITUTION: The objective liquid agent contains a mixed aqueous solution of (A) at least one kind of resin selected from styrene-acrylic acid resin, styrene-acrylic acid-acrylic acid ester resin, styrene-maleic acid resin, styrene-maleic acid-maleic acid half-ester resin, (di) isobutylene-maleic acid resin and (di) isobutylene-maleic acid-maleic acid half-ester resin and (B) an acrylamide resin produced by reacting (a) an acrylamide compound with (b) an anionic vinyl monomer in the presence of (c) a urea compound.

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CLAIMS

[Claim(s)]

[Claim 1] Styrene-acrylic acid resin, styrene-acrylic-acid-acrylic ester resin, Styrene-maleic resin, styrene-maleic-acid-maleic-acid half ester resin,

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] the front face which this invention raises the surface reinforcement of paper, internal reinforcement, and a size effect with sufficient balance, and is excellent in product stability -- quality of paper -- it is related with improvement liquids and solutions.

[0002]

[Description of the Prior Art] Development of a printing technique in recent years is remarkable, and improvement in printabilities, such as an advanced demand, for example, surface reinforcement, internal reinforcement, and size nature, has come to be called for from a print sheet with improvement in the speed of printing, and quality improvement. Since it corresponds to these demands, the chemical for paper manufacture is added to the aqueous slurry of pulp (internal), or carrying out coating (outside **) on the surface of paper is performed. Among these, an internal agent does not have the enough yield of a chemical and, on the other hand, it is known that the yield of an external additive of a chemical is more advantageous from being about 100% and carrying out a direct action on the surface of paper.

[0003] the front face aiming at raising the surface reinforcement of paper, internal reinforcement, and size nature, and raising a printability -- quality of paper -- as an improver, the mixture (JP,60-10160,B) of alkenyl succinate and the polyacrylamide system matter is known conventionally. moreover, the front face excellent in the improvement in the surface reinforcement of paper, internal reinforcement, a water resisting property, etc. -- quality of paper -- the polyacrylamide system resin (JP,5-302298,A) obtained by carrying out the polymerization of the anionic vinyl monomer to acrylamide under existence of ureas as an improver is known.

[0004]

[Problem(s) to be Solved by the Invention] however, the latest advanced front face -- quality of paper -- the demand of improvement -- receiving -- the conventional front face -- quality of paper -- the improver of the point of effectiveness satisfactory enough not being acquired but raising surface reinforcement, internal reinforcement, and size nature with sufficient balance especially was inadequate. for example, non-size paper -- the front face of the above-mentioned conventional technique (JP,60-10160,B) -- quality of paper -- although surface reinforcement and internal reinforcement improve when surface coating of the improver is carried out by the gate roll coater, size press, etc. -- the improvement in size nature -- enough -- **** -- it cannot say. Moreover, when coating is carried out like strong size paper, a size effect may not improve, but may fall rather and is regarded as questionable.

[0005] then, a size effect is improved -- it should make -- the front face of the above-mentioned conventional technique (JP,60-10160,B) -- quality of paper -- the mixing ratio of the hydrophobic component (alkenyl succinate) of an improver -- if a rate is made to increase, size nature will improve, but on the other hand, since surface reinforcement and internal reinforcement fall remarkably, they are not desirable. Moreover, the method of raising own (alkenyl succinate) hydrophobicity of a hydrophobic component, and heightening a size effect, without changing the above-mentioned mixed ratio, brings about the fall of compatibility with the

polyacrylamide system matter used together and is not desirable.

[0006] Moreover, the polyacrylamide system resin (JP,5-302298,A) obtained by carrying out the polymerization of the anionic vinyl monomer to acrylamide under existence of ureas does not have the enough size disposition top effectiveness, although the effectiveness of raising the surface reinforcement of paper and internal reinforcement is excellent. for this reason, the front face which raises size nature with sufficient balance with surface reinforcement and internal reinforcement -- quality of paper -- an appearance of an improver was desired strongly. a front face for this invention to solve the above-mentioned technical problem -- quality of paper -- improvement liquids and solutions are offered.

[0007]

[Means for Solving the Problem] As a result of inquiring wholeheartedly in order to reply to the request, this invention person etc. Styrene-acrylic acid resin, Styrene-acrylic-acid-acrylic ester resin, styrene-maleic resin, At least a kind of resin chosen from the group which consists of styrene-maleic-acid-maleic-acid half ester resin, (**) isobutylene-maleic resin, and (**) isobutylene-maleic-acid-maleic-acid half ester resin [A], the front face containing the mixed water solution of the acrylamide system resin [B] reacted and obtained in a cross linking agent (d) under existence of ureas (a) acrylamides (b), an anionic vinyl monomer (c), and if needed -- quality of paper -- using improvement liquids and solutions -- surface reinforcement -- It finds out raising a size effect with sufficient balance with internal reinforcement, and came to complete this invention.

[0008] This invention Namely, styrene-acrylic acid resin, styrene-acrylic-acid-acrylic ester resin, Styrene-maleic resin, styrene-maleic-acid-maleic-acid half ester resin, (**) -- isobutylene-maleic resin and (**) -- at least under a kind of resin [A] chosen from the group which consists of isobutylene-maleic-acid-maleic-acid half ester resin, and existence of ureas (a) the front face containing the mixed water solution of acrylamides (b) and the acrylamide system resin [B] reacted and obtained in an anionic vinyl monomer (c) -- quality of paper -- improvement liquids and solutions, [0009] Or styrene-acrylic acid resin, styrene-acrylic-acid-acrylic ester resin, Styrene-maleic resin, styrene-maleic-acid-maleic-acid half ester resin, (**) -- isobutylene-maleic resin and (**) -- at least under a kind of resin [A] chosen from the group which consists of isobutylene-maleic-acid-maleic-acid half ester resin, and existence of ureas (a) acrylamides (b), and an anionic vinyl monomer (c) and the front face containing the mixed water solution of the acrylamide system resin [B] reacted and obtained in a cross linking agent (d) -- quality of paper -- improvement liquids and solutions are offered.

[0010] As opposed to the (Acrylamide b) 100 weight section the above-mentioned resin [A] In addition, 1 - 50 weight section, In ureas (a), the 5 - 100 weight section and an anionic vinyl monomer (c) receive 0.5 - 50 weight section or the (Acrylamide b) 100 weight section. It is desirable that the 5 - 100 weight section and an anionic vinyl monomer (c) are [the above-mentioned resin [A] / 0.5 - 50 weight section and a cross linking agent (d)] 0.005 - 10 weight sections for 1 - 50 weight section and ureas (a).

[0011] Furthermore, it is desirable that the above-mentioned resin [A] is styrene-acrylic acid resin, and it is desirable that the above-mentioned acrylamides (b) are acrylamide and methacrylamide. Moreover, the thing which was chosen from the group which the above-mentioned anionic vinyl monomer (c) becomes from partial saturation monocarboxylic acid, partial saturation dicarboxylic acid, partial saturation tricarboxylic acid, partial saturation tetracarboxylic acid, a partial saturation sulfonic acid, partial saturation phosphonic acid, and those salts and which is a kind at least is desirable.

[0012] Next, this invention is explained to a detail. Although what carried out the polymerization by which approaches, such as a bulk polymerization, solution polymerization, and an emulsion polymerization, is sufficient as the styrene-acrylic acid resin which is resin of the [A] component used by this invention, styrene-acrylic-acid-acrylic ester resin, styrene-maleic resin, styrene-maleic-acid-maleic-acid half ester resin, (**) isobutylene-maleic resin, and (**) isobutylene-maleic-acid-maleic-acid half ester resin, especially its bulk-polymerization article is desirable. To use powdered resin, it is necessary to saponify in order to consider as a water solution in front of a polymerization or during a polymerization.

[0013] As alkali used at the time of saponification, organic [one sort or two sorts or more of] or the inorganic alkali chosen from a sodium hydroxide, a potassium hydroxide, ammonia, a specific silicate, a sodium aluminate, monoethanolamine, triethanolamine, etc. can be used. Moreover, about the presentation ratio of styrene, an acrylic acid and styrene, an acrylic acid, acrylic ester and styrene, a maleic acid and styrene, a maleic acid, maleic-acid half ester and a (**)
isobutylene, a maleic acid and a (**) isobutylene, a maleic acid, and maleic-acid half ester, and molecular weight, if it is within the limits which does not check compatibility with acrylamide system resin [B], it will not limit especially.

[0014] As resin [A], GSA2302 (styrene-acrylic acid resin: the Gifu shellac company make), GSA2303 (styrene-acrylic-acid-acrylic-ester resin: the Gifu shellac company make), SMA3000 (styrene-maleic resin: Elf Atochem make), SMA2000 (styrene-maleic resin: Elf Atochem make), the iso van 10 (isobutylene-maleic resin: Kuraray Co., Ltd. make), etc. are mentioned. Especially, styrene-acrylic acid resin is desirable.

[0015] Next, the acrylamide system resin [B] used by this invention is explained. As ureas of the (a) component used for acrylamide system resin [B], although a urea, thiourea, an ethylene urea, ethylenetiourea, etc. are mentioned, especially a urea is desirable.

[0016] As acrylamides of the (b) component used for acrylamide system resin [B], it is desirable, and acrylamide and methacrylamide can also use any one or more sorts of the N permutation acrylamides, such as N-methyl (meta) acrylamide, N-ethyl (meta) acrylamide, N, and N-dimethyl (meta) acrylamide, N-isopropyl (meta) acrylamide, and N-t-octyl (meta) acrylamide, using them together with acrylamide and methacrylamide.

[0017] It illustrates below about the partial saturation monocarboxylic acid which is the anionic vinyl monomer of the (c) component used for acrylamide system resin [B], partial saturation dicarboxylic acid, partial saturation tricarboxylic acid, partial saturation tetracarboxylic acid, a partial saturation sulfonic acid, partial saturation phosphonic acid, and those salts.

[0018] As partial saturation monocarboxylic acid and those salts, alkali-metal salts or ammonium salt, such as an acrylic acid, methacrylic acids and those sodium, and potassium salt, etc. are mentioned.

[0019] As partial saturation dicarboxylic acid and those salts, alkali-metal salts or ammonium salt, such as a maleic acid, a fumaric acid, an itaconic acid, citraconic acids and those sodium, and potassium salt, etc. are mentioned.

[0020] As partial saturation tricarboxylic acid and those salts, they are aconitic acid, 3-butene-1, 2, 3-tricarboxylic acid, and 4-pentene. - Alkali-metal salts or ammonium salt, such as 1, 2, and 4-tricarboxylic acid and those sodium, and potassium salt, etc. are mentioned.

[0021] As partial saturation tetracarboxylic acid and those salts, it is 1-pentene. - They are 1, 1, 4, and 4-tetracarboxylic acid and 4-pentene. - They are 1, 2, 3, 4-tetracarboxylic acid, and 3-hexene. - Alkali-metal salts or ammonium salt, such as 1, 1, 6, and 6-tetracarboxylic acid and those sodium, and potassium salt, etc. are mentioned.

[0022] As a partial saturation sulfonic acid, alkali-metal salts or ammonium salt, such as a vinyl sulfonic acid, a styrene sulfonic acid, an allyl compound sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid and those sodium, and potassium salt, etc. are mentioned.

[0023] As partial saturation phosphonic acid, alkali-metal salts or ammonium salt, such as vinyl phosphonic acid, alpha-phenyl vinyl phosphonic acid and those sodium, and potassium salt, etc. are mentioned.

[0024] An itaconic acid, an acrylic acid, and its salts are desirable among the above-mentioned anionic vinyl monomers, and an itaconic acid and its salts are desirable especially. The approach of introducing an anion radical can also be used by hydrolyzing acrylamide system resin [B] with an acid or alkali in addition to the approach using an anionic vinyl monomer as the introductory approach of an anionic radical.

[0025] The Nonion nature vinyl monomer of the amount of extent which does not injure the compatibility of the cationic vinyl monomer of dimethylaminopropyl (meta) acrylamide, the 4th class ghost of its, etc. which can be copolymerized, or the obtained resin constituent, and water solubility other than the above (a), (b), and the (c) component can also be used.

[0026] As a cationic vinyl monomer, for example Dimethylaminoethyl (meta) acrylate,

Diethylaminoethyl (meta) acrylate, dimethylaminopropyl (meta) acrylate, Diethylamino propyl (meta) acrylate, dimethylaminopropyl (meta) acrylamide, or diethylamino propyl (meta) acrylamide, Salts of inorganic acids, such as vinyl monomers which have the 3rd class amino groups, such as an alkyl diaryl amine, dialkyl allylamine, a diaryl amine, and allylamine, the 2nd class amino group, and the 1st class amino group or those salts, a sulfuric acid, a formic acid, and an acetic acid, or an organic acid, [0027] Or alkyl halide, such as this the 3rd class amino-group content vinyl monomer, methyl chloride, and a methyl bromide, Aryl AKIRU halide, such as benzyl chloride and a benzyl star's picture, A dimethyl sulfate, a diethyl sulfate, epichlorohydrin, 3-chloro-2-hydroxypropyl trimethylammoniumchloride, The vinyl monomer containing the quarternary ammonium salt obtained by the reaction with the 4th class-ized agents, such as glycidyl trialkyl ammonium chloride, For example, 2-hydroxy - N, N, N, N', N'-pentamethyl-N'-[3-((1-oxo-2-propenyl) amino) propyl]-1, and 3-pro pansy aminium dichloride etc. is illustrated. It is independent in these kinds, or two or more sorts can be used together and used.

[0028] As an Nonion nature vinyl monomer, acrylonitrile, meta-acrylonitrile, styrene, the methyl vinyl ether, the alkyl ester of an acrylic acid (meta), 2-hydroxy ester, or glycidyl ester is illustrated, it is independent in these kinds, or two or more sorts can be used together and used.

[0029] As a cross linking agent of the (d) component used for acrylamide system resin [B] Ethylene GURIKORUJI (meta) acrylate, diethylene GURIKORUJI (meta) acrylate, Di(meth) acrylate, such as TORIECHIRENGURIKORUJI (meta) acrylate and propylene GURIKORUJI (meta) acrylate GURISERINJI (meta) acrylate, a trimethylol propane ethyleneoxide addition product thoria chestnut rate, Methylenebis (meta) acrylamide, ethylene screw (meta) acrylamide, Screw (meta) acrylamides, such as - bis-acrylamide acetic-acid, and N,N, N'-bis-acrylamide methyl-acetate, N, and N-benzylidene bis-acrylamide, [hexa methylenebis (meta) acrylamide N, and] [0030] Divinyl ester, such as an adipic-acid divinyl and a sebacic-acid divinyl Epoxy acrylate, urethane acrylate, allyl compound (meta) acrylate, Diallyl phthalate, diallyl maleate, diaryl succinate, diaryl acrylamide, Divinylbenzene, diisopropylbenzene, N, and N-diaryl methacrylamide, 2 functionality vinyl monomers, such as diaryl dimethylammonium, diallyl chlorendate, and glycidyl (meta) acrylate, 3 functionality vinyl monomers, such as 1, 3, 5-thoria chestnut roil hexahydro-S-triazine, triallyl isocyanurate, N, and N-diaryl acrylamide, a triaryl amine, and triallyl trimellitate, [0031] Tetramethylolmethane tetraacrylate, tetra-allyl compound pyromellitate, N, N, N', and N' - tetra-allyl compound-1,4-diaminobutane and a tetra-allylamine salt -- 4 functionality vinyl monomers, such as tetra-allyloxy ethane, tetramethylolmethane-tree beta-aziridinyl propionate, Trimethylol propane-tree beta-AJIRIJINIRUPUROPIONETO, Water-soluble aziridinyl compounds, such as 4 and 4'-screw (ethyleneimine carbonylamino) diphenylmethane, (Pori) Water-soluble polyfunctional epoxy compounds, such as ethylene glycol diglycidyl ether, propylene glycol (Pori) diglycidyl ether, glycerol (Pori) diglycidyl ether, and glycerol triglycidyl ether (Pori), [0032] And 3-(meta) acryloxy methyl trimethoxysilane, 3-(meta) acryloxypropyl dimethoxymethylsilane, 3-(meta) acryloxypropyltrimethoxysilane, 3-(meta) acryloxy propylmethyl dichlorosilane, 3-(meta) acryloxy octadecyl triacetoxysilane, 3-(meta) acryloxy -2, 5-dimethyl hexyl diacetoxymethylsilane, 3-(meta) acrylamide propyltrimethoxysilane, 2-(meta) acrylamide ethyl trimethoxysilane, 1-(meta) acrylamide methyl trimethoxysilane, 2-(meta) acrylamide-2-methylpropyl trimethoxysilane, 2-(meta) acrylamide-2-methylethyl trimethoxysilane, [0033] 2-(meta) acrylamide isopropyl trimethoxy silane, 3-(meta) acrylamide propyl triethoxysilane, N-(2-(meta) acrylamide ethyl) aminopropyl trimethoxysilane, Oxy-propyltrimethoxysilane, (3-(meta) acrylamide propyl) 3-(N-methyl (meta) acrylamide) propyltrimethoxysilane, 3-(meta) (acrylamide-methoxy)-3-hydroxypropyl trimethoxysilane, 3-(meta) (acrylamide-methoxy) propyltrimethoxysilane, 3-(vinylbenzyl aminopropyl) trimethoxysilane, [0034] Dimethyl-3-(meta) acrylamide-propyl -3 -(trimethoxysilyl)- Propyl ammoniumchloride, Dimethyl-2-(meta) acrylamide-2-methylpropyl -3 -(trimethoxysilyl)- Propyl ammoniumchloride, 3-(meta) acrylamide propylmethyl dimethoxysilane, 3-(meta) acrylamide propyl dimethyl METOKISHISHIRAN, 3-(meta) acrylamide propyl isobutyl dimethoxysilane, 2-(meta) acrylamide propyl isobutyl dimethoxysilane, 2-(meta) acrylamide-2-methyl propyl monochloro dimethoxysilane, 2-(meta) acrylamide-2-methylpropyl hydrogen dimethoxysilane, [0035] 3-(meta) acrylamide propylbenzyl diethoxysilane, 3-(meta) acrylamide propyl

triacetoxysilane, 2-(meta) acrylamide ethyl triacetoxysilane, 4-(meta) acrylamide butyl triacetoxysilane, 2-(meta)acrylamide-2-methylpropyltriacetoxysilane, N-(2-(meta) acrylamide ethyl) aminopropyl triacetoxysilane, 2-(N-ethyl (meta) acrylamide) ethyl triacetoxysilane, 3-(meta) acrylamide propyl OKUCHIRUJI acetoxysilane, 1-(meta) acrylamide methylphenyl diacetoxysilane, [0036] 3-(meta) acrylamide propyltripropionyloxy silane, 3-(meta) acrylamide pro PIRUTORI (N-methylaminoethoxy) silane, Vinyl trichlorosilane, vinyl methyl dichlorosilane, divinyl dichlorosilane, Vinyl phenyl dichlorosilane, vinyl dimethyl chlorosilane, vinyl methylphenyl chlorosilane, Vinyl diphenyl chlorosilane, vinyltrimetoxysilane, vinyl methyl dimethoxysilane, Vinyl isobutyl dimethoxysilane, a vinyl dimethyl methoxy silane, vinyltriethoxysilane, 3-vinylbenzyl aminopropyl triethoxysilane, vinyl methyl diethoxysilane, [0037] Divinyl diethoxysilane, a vinyl dimethylethoxy silane, a vinyl diphenyl ethoxy silane, A vinyl triisopropoxy silane, BINIRUTORI butoxysilane, vinyl dimethyl iso butoxysilane, Vinyl triphenoxysilane, a vinyl dimethyl (3-amino phenoxy) silane, A vinyl dimethyl (4-amino phenoxy) silane, a vinyl dimethyl (3-methyl-4-chloro phenoxy) silane, Silicon system compounds, such as a vinyl dimethyl (2-methyl-4-chloro phenoxy) silane, vinyltriacetoxysilane, a vinyl methyl diacetoxysilane, and vinyl dimethyl acetoxysilane, can be illustrated.

[0038] the front face of this invention -- quality of paper -- improvement liquids and solutions can be obtained by mixing resin [A] and acrylamide system resin [B] with a conventional method. The amount of the resin [A] used has desirable 1 - 50 weight section to the (Acrylamide b) 100 weight section used for acrylamide system resin [B], and especially its 3 - 30 weight section is desirable. The weight ratio of each component (a), (c), and (d) used for the reaction of the acrylamide system resin [B] of this invention As opposed to the (Acrylamide b) 100 weight section ureas (a) The 5 - 100 section, The ten to 60 section, it is the ten to 30 section still more preferably, and an anionic vinyl monomer (c) is the 2 - 20 section preferably the 0.5 to 50 section, and a cross linking agent (d) is the 0.01 - 2 section preferably the 0.005 to 10 section.

[0039] When the weight ratio of resin [A], ureas (a), and an anionic vinyl monomer (c) is except this range, surface reinforcement, internal reinforcement, and a size effect cannot be raised with sufficient balance, and it is not desirable. Moreover, when the weight ratio of a cross linking agent (d) exceeds this range, product viscosity is high and is not desirable.

[0040] Composition of the acrylamide system resin [B] used by this invention can be conventionally performed by various well-known approaches. For example, in a predetermined reaction container, two to 40% of the weight, monomer concentration can prepare each component and water so that it may become 5 - 30% of the weight preferably, it can add a polymerization initiator, and can obtain the acrylamide system resin [B] which is 40-100 degrees C in temperature under stirring, and is made into the purpose by performing the reaction of 0.5 - 10 hours. Of course, acrylamides (b), an anionic vinyl monomer (c), and a cross linking agent (d) component can also perform continuation dropping etc. according to the description of the component to be used.

[0041] Especially the polymerization initiator used for composition of the acrylamide system resin [B] of this invention is not limited, and the thing of well-known common use can be used for it. For example, radical polymerization initiators, such as sodium persulfate, potassium persulfate, ammonium persulfate, a hydrogen peroxide, and the second cerium salt, are used 0.01 to 5% of the weight to the sum total weight of acrylamides (b) and an anionic vinyl monomer (c). Moreover, the redox polymerization of the reducing agents, such as dimethylamine, a sodium hydrogensulfite, and sodium formaldehyde sulfoxylate, can also be used together and carried out.

[0042] Moreover, the chain transfer agent of well-known common use may be used if needed. For example, allyl compounds, such as allyl alcohol and allylamine, mercaptoethanol, thioglycolic acid, its alkali-metal salt or ammonium salt, isopropyl alcohol, sodium hypophosphite, etc. are mentioned.

[0043] the front face of this invention -- quality of paper -- additives, such as a non-skid agent, a release agent, a rust-proofer, antiseptics, a defoaming agent, a viscosity controlling agent, a color, a surface sizing compound, and water repellent, may be added to the coating liquid containing improvement liquids and solutions or this. moreover, nature, such as starch, polyvinyl

alcohol, and a carboxymethyl cellulose, or concomitant use with synthetic macromolecule, and the front face of further others -- quality of paper -- concomitant use with an improver is not restricted, either. In addition, as for the solid content concentration of coating liquid, it is desirable to usually be carried out at 0.1 - 15%.

[0044] the front face of this invention -- quality of paper -- it is desirable to carry out the surface coating liquid containing improvement liquids and solutions by the approach of size press, a film press, a gate roll coater, a blade coating machine, or a calender in carrying out coating to paper or the paper board. Moreover, coating can also be carried out by the bar coating machine, the knife coating machine, an air knife coater, etc.

[0045] moreover, the front face of this invention -- quality of paper -- coating of the coating liquid containing improvement liquids and solutions can be carried out to acid paper or alkaline paper. As a class of acid paper or alkaline paper, various stencil paper, such as coat stencil paper, a newsprint, a liner, a coat ball, printing writing paper, a form form, a PPC form, inkjet printing paper, a hot printing form, and a thermal paper, is mentioned. Although also whenever [size / of stencil paper] is arbitrary, when carrying out coating using size press etc., it is desirable to use an internal sizing compound in order to adjust the liquid adsorption of stencil paper.

[0046]

[Example] Although an example and the example of a comparison are given and this invention is hereafter explained to a detail, this invention is not limited to the following example. In addition, the section and especially % mean weight section and weight %, as long as there is no notice.

[0047] The synthetic example 1 (composition of acrylamide system resin [B])

The water 328 section, the urea 20 section, the 50% acrylamide water-solution 200 section, the itaconic-acid 4 section, and the isopropyl alcohol 35 section were taught to the 1l. 4 opening flask which attached an agitator, a thermometer, a reflux cooling pipe, and nitrogen gas installation tubing, and the temperature up was carried out to 60 degrees C. Subsequently, the ammonium persulfate water-solution 3.3 section was added 5% under nitrogen gas installation, the temperature up was carried out to 80 degrees C, and it was made to react for 2 hours. The water 30 section was added to the acquired resultant, and the water soluble resin of the solid content of 20.6%, the viscosity of 5500cps, and pH7.2 was obtained. Let this be Resin m.

[0048] Except changing suitably a class and the amount used, such as the synthetic example 2 - 7 ureas (a), acrylamides (b), an anionic vinyl monomer (c), and a cross linking agent (d), as Table 1, it carried out like the synthetic example 1 and resin n-s was obtained.

[0049] The 124 sections and 20% aqueous ammonia solution of GSA2302 (styrene-acrylic acid resin) were mixed by solid content conversion, and the ten sections were mixed for example 1 resin m by solid content conversion. Let the obtained mixed water solution be Resin M.

[0050] The resin [A] and acrylamide system resin [B] which are shown in one to examples 2-6 and example of comparison 5 table 2 were mixed like the example 1, and resin N-R and resin w-z (example of a comparison) were obtained. Moreover, let the case of Resin m be the example 1 of a comparison.

[0051] Example 7 above-mentioned resin M-R, Resin m, and w-z (example of a comparison) were diluted with water, and the coating liquid whose solid content concentration is 3% was prepared. The No.3 bar coating machine was used for the non-coating newsprint (basis weight 45 [g/m²]), and one side coating of this coating liquid was carried out to it, and it was dried with the drum dryer (for 80 degrees C and 50 seconds). Gas conditioning was carried out after desiccation for 24 hours in 20 degrees C and the air conditioned room of 65% of relative humidity, and various evaluation trials were presented after that. A result is shown in Table 3. In addition, the example which carried out coating only of the water was indicated to Table 3.

[0052] In addition, the evaluation trial was performed by the following measuring methods. Surface reinforcement: Dry pick ; RI printing testing-machine, and nip width-of-face ink [of 10mm]:FINE INK. (Dainippon Ink & Chemicals make)

The paper after ink T.V.=20 or 24 printings turned, the condition was observed with the naked eye, and five-step evaluation was performed by making 1 into **, having made 5 as A.

internal: on the strength -- SUKOTTO bond (kgf-cm); -- it measured on the bond strength of

5kg/cm², and the conditions for 30 seconds using the internal bond tester (Kumagaya Riki Kogyo K.K. make).

size whenever: -- drop test (second); -- J.TAPPI It carried out according to 33 (water 5microl).
[0053] Double-sided coating (whenever [part / for // and 100m coating solution temperature / in nip pressure 20 kg/cm and coating rate] 50 degrees C) of the coating liquid prepared like example 8 example 7 was carried out to non-coating neutral paper of fine quality (basis weight 82 [g/m²]) with the size press equipment for a trial (Kumagaya Riki Kogyo K.K. make), and it dried with the drum dryer (for 80 degrees C and 50 seconds). Measurement of the surface reinforcement of each coated paper, internal reinforcement, and size nature was performed like the example 7 after desiccation. A result is shown in Table 4.

[0054]

[Table 1]

表 1 アクリルアミド系樹脂 (B) の合成

	尿素類 (a)	アクリル アミド類 (b)	アニオン性 ビニルモノマー (c)	架橋剤 (d)	その他の モノマー	固形分 (%)	粘度 (c p s)	pH
合成例 1 樹脂 m	尿素 20	AAm 100	IA 4	—		20.6	5500	7.2
2 n	尿素 20	AAm 100	ViP / IA 3/1	—		20.1	5400	7.6
3 o	尿素 10	AAm 100	AMPS 3	—	AN10	20.5	6200	7.6
4 p	尿素 30	AAm 90 / MAAm 10	AA 10	—		20.2	5500	7.7
5 q	尿素 15 / チオ尿素 5	AAm 100	IA 2	MBAAm 0.1		20.6	4900	7.2
6 r	尿素 20	AAm 100	—	—		20.3	5500	7.1
7 s	—	AAm 100	IA 4	—		20.1	5300	7.3

表中の略号は下記の通りである。なお、表中の各成分の単位は重量部である。

AAm: アクリルアミド、MAAm: メタクリルアミド、IA: イタコン酸、ViP: ビニルホスホン酸、
AMPS: 2-アクリルアミド-2-メチルプロパンスルホン酸、AA: アクリル酸、AN: アクリロニトリル、
MBAAm: メチレンビスアクリルアミド、

[0055]

[Table 2]

表 2 実施例 1～6、比較例 1～5

	樹脂 [A]	重量部 (固形分換算)	アクリルアミド系樹脂 [B]	重量部 (固形分換算)
実施例 1 樹脂 m	GSA2302	10	樹脂 m	124
2 N	SMA3000	5	m	124
3 O	GSA2302	10	n	124
4 P	SMA2000	20	o	123
5 Q	イソバン10	20	p	140
6 R	GSA2303	10	q	122
比較例 1 樹脂 m	—	—	m	124
2 w	GSA2302	10	r	120
3 x	GSA2302	10	s	104
4 y	SMA3000	60	m	124
5 z	ドデセニル無水コハク酸	10	m	124

表中の略号は下記の通りである。

GSA2302 : スチレン-アクリル酸樹脂
GSA2303 : スチレン-アクリル酸-アクリル酸エステル樹脂
SMA3000 : スチレン-マレイン酸樹脂
SMA2000 : スチレン-マレイン酸樹脂
イソバン10 : イソブチレン-マレイン酸樹脂

[0056]

[Table 3]

表 3 実施例 7

	樹脂	表面強度	内部強度 (kgf/cm)	サイズ度 (秒)
		ドライピック	スコットボンド	ドロップテスト
本 発 明	M	5	2.51	81
	N	5	2.53	75
	O	4	2.41	80
	P	4	2.45	85
	Q	4	2.40	68
	R	5	2.51	83
比 較	m	5	2.54	22
	w	3	2.15	79
	x	3	2.19	77
	y	3	2.11	91
	z	2	2.03	35
	水	1	1.51	20

[0057]

[Table 4]

表 4 実施例 8

	樹脂	表面強度	内部強度 (kgf/cm)	サイズ度 (秒)
		ドライピック	スコットボンド	ドロップテスト
本 発 明	M	5	3.14	87
	N	5	3.20	75
	O	4	3.01	88
	P	4	3.06	92
	Q	4	3.07	78
	R	5	3.15	85
比 較	m	5	3.16	8
	w	3	2.80	81
	x	3	2.85	87
	y	3	2.77	98
	z	2	2.63	33
	水	1	2.51	7

[0058]

[Effect of the Invention] the front face of this invention -- quality of paper -- by using improvement liquids and solutions, it became possible with the conventional technique to raise the surface reinforcement of paper without nothing profit, internal reinforcement, and a size effect with sufficient balance:

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EFFECT OF THE INVENTION

[Effect of the Invention] the front face of this invention -- quality of paper -- by using improvement liquids and solutions, it became possible with the conventional technique to raise the surface reinforcement of paper without nothing profit, internal reinforcement, and a size effect with sufficient balance.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] however, the latest advanced front face -- quality of paper -- the demand of improvement -- receiving -- the conventional front face -- quality of paper -- the improver of the point of effectiveness satisfactory enough not being acquired but raising surface reinforcement, internal reinforcement, and size nature with sufficient balance especially was inadequate. for example, non-size paper -- the front face of the above-mentioned conventional technique (JP,60-10160,B) -- quality of paper -- although surface reinforcement and internal reinforcement improve when surface coating of the improver is carried out by the gate roll coater, size press, etc. -- the improvement in size nature -- enough -- *** -- it cannot say. Moreover, when coating is carried out like strong size paper, a size effect may not improve, but may fall rather and is regarded as questionable.

[0005] then, a size effect is improved -- it should make -- the front face of the above-mentioned conventional technique (JP,60-10160,B) -- quality of paper -- the mixing ratio of the hydrophobic component (alkenyl succinate) of an improver -- if a rate is made to increase, size nature will improve, but on the other hand, since surface reinforcement and internal reinforcement fall remarkably, they are not desirable. Moreover, the method of raising own (alkenyl succinate) hydrophobicity of a hydrophobic component, and heightening a size effect, without changing the above-mentioned mixed ratio, brings about the fall of compatibility with the polyacrylamide system matter used together and is not desirable.

[0006] Moreover, the polyacrylamide system resin (JP,5-302298,A) obtained by carrying out the polymerization of the anionic vinyl monomer to acrylamide under existence of ureas does not have the enough size disposition top effectiveness, although the effectiveness of raising the surface reinforcement of paper and internal reinforcement is excellent. for this reason, the front face which raises size nature with sufficient balance with surface reinforcement and internal reinforcement -- quality of paper -- an appearance of an improver was desired strongly. a front face for this invention to solve the above-mentioned technical problem -- quality of paper -- improvement liquids and solutions are offered.

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MEANS

[Means for Solving the Problem] As a result of inquiring wholeheartedly in order to reply to the request, this invention person etc. Styrene-acrylic acid resin, Styrene-acrylic-acid-acrylic ester resin, styrene-maleic resin, At least a kind of resin chosen from the group which consists of styrene-maleic-acid-maleic-acid half ester resin, (**) isobutylene-maleic resin, and (**) isobutylene-maleic-acid-maleic-acid half ester resin [A], the front face containing the mixed water solution of the acrylamide system resin [B] reacted and obtained in a cross linking agent (d) under existence of ureas (a) acrylamides (b), an anionic vinyl monomer (c), and if needed -- quality of paper -- using improvement liquids and solutions -- surface reinforcement -- It finds out raising a size effect with sufficient balance with internal reinforcement, and came to complete this invention.

[0008] This invention Namely, styrene-acrylic acid resin, styrene-acrylic-acid-acrylic ester resin, Styrene-maleic resin, styrene-maleic-acid-maleic-acid half ester resin, (**) -- isobutylene-maleic resin and (**) -- at least under a kind of resin [A] chosen from the group which consists of isobutylene-maleic-acid-maleic-acid half ester resin, and existence of ureas (a) the front face containing the mixed water solution of acrylamides (b) and the acrylamide system resin [B] reacted and obtained in an anionic vinyl monomer (c) -- quality of paper -- improvement liquids and solutions, [0009] Or styrene-acrylic acid resin, styrene-acrylic-acid-acrylic ester resin, Styrene-maleic resin, styrene-maleic-acid-maleic-acid half ester resin, (**) -- isobutylene-maleic resin and (**) -- at least under a kind of resin [A] chosen from the group which consists of isobutylene-maleic-acid-maleic-acid half ester resin, and existence of ureas (a) acrylamides (b), and an anionic vinyl monomer (c) and the front face containing the mixed water solution of the acrylamide system resin [B] reacted and obtained in a cross linking agent (d) -- quality of paper -- improvement liquids and solutions are offered.

[0010] As opposed to the (Acrylamide b) 100 weight section the above-mentioned resin [A] In addition, 1 - 50 weight section, In ureas (a), the 5 - 100 weight section and an anionic vinyl monomer (c) receive 0.5 - 50 weight section or the (Acrylamide b) 100 weight section. It is desirable that the 5 - 100 weight section and an anionic vinyl monomer (c) are [the above-mentioned resin [A] / 0.5 - 50 weight section and a cross linking agent (d)] 0.005 - 10 weight sections for 1 - 50 weight section and ureas (a).

[0011] Furthermore, it is desirable that the above-mentioned resin [A] is styrene-acrylic acid resin, and it is desirable that the above-mentioned acrylamides (b) are acrylamide and methacrylamide. Moreover, the thing which was chosen from the group which the above-mentioned anionic vinyl monomer (c) becomes from partial saturation monocarboxylic acid, partial saturation dicarboxylic acid, partial saturation tricarboxylic acid, partial saturation tetracarboxylic acid, a partial saturation sulfonic acid, partial saturation phosphonic acid, and those salts and which is a kind at least is desirable.

[0012] Next, this invention is explained to a detail. Although what carried out the polymerization by which approaches, such as a bulk polymerization, solution polymerization, and an emulsion polymerization, is sufficient as the styrene-acrylic acid resin which is resin of the [A] component used by this invention, styrene-acrylic-acid-acrylic ester resin, styrene-maleic resin, styrene-maleic-acid-maleic-acid half ester resin, (**) isobutylene-maleic resin, and (**) isobutylene-

maleic-acid-maleic-acid half ester resin, especially its bulk-polymerization article is desirable. To use powdered resin, it is necessary to saponify in order to consider as a water solution in front of a polymerization or during a polymerization.

[0013] As alkali used at the time of saponification, organic [one sort or two sorts or more of] or the inorganic alkali chosen from a sodium hydroxide, a potassium hydroxide, ammonia, a specific silicate, a sodium aluminate, monoethanolamine, triethanolamine, etc. can be used. Moreover, about the presentation ratio of styrene, an acrylic acid and styrene, an acrylic acid, acrylic ester and styrene, a maleic acid and styrene, a maleic acid, maleic-acid half ester and a (**)
isobutylene, a maleic acid and a (**) isobutylene, a maleic acid, and maleic-acid half ester, and molecular weight, if it is within the limits which does not check compatibility with acrylamide system resin [B], it will not limit especially.

[0014] As resin [A], GSA2302 (styrene-acrylic acid resin: the Gifu shellac company make), GSA2303 (styrene-acrylic-acid-acrylic-ester resin: the Gifu shellac company make), SMA3000 (styrene-maleic resin: Elf Atochem make), SMA2000 (styrene-maleic resin: Elf Atochem make), the iso van 10 (isobutylene-maleic resin: Kuraray Co., Ltd. make), etc. are mentioned. Especially, styrene-acrylic acid resin is desirable.

[0015] Next, the acrylamide system resin [B] used by this invention is explained. As ureas of the (a) component used for acrylamide system resin [B], although a urea, thiourea, an ethylene urea, ethylenetiourea, etc. are mentioned, especially a urea is desirable.

[0016] As acrylamides of the (b) component used for acrylamide system resin [B], it is desirable, and acrylamide and methacrylamide can also use any one or more sorts of the N permutation acrylamides, such as N-methyl (meta) acrylamide, N-ethyl (meta) acrylamide, N, and N-dimethyl (meta) acrylamide, N-isopropyl (meta) acrylamide, and N-t-octyl (meta) acrylamide, using them together with acrylamide and methacrylamide.

[0017] It illustrates below about the partial saturation monocarboxylic acid which is the anionic vinyl monomer of the (c) component used for acrylamide system resin [B], partial saturation dicarboxylic acid, partial saturation tricarboxylic acid, partial saturation tetracarboxylic acid, a partial saturation sulfonic acid, partial saturation phosphonic acid, and those salts.

[0018] As partial saturation monocarboxylic acid and those salts, alkali-metal salts or ammonium salt, such as an acrylic acid, methacrylic acids and those sodium, and potassium salt, etc. are mentioned.

[0019] As partial saturation dicarboxylic acid and those salts, alkali-metal salts or ammonium salt, such as a maleic acid, a fumaric acid, an itaconic acid, citraconic acids and those sodium, and potassium salt, etc. are mentioned.

[0020] As partial saturation tricarboxylic acid and those salts, they are aconitic acid, 3-butene-1, 2, 3-tricarboxylic acid, and 4-pentene. - Alkali-metal salts or ammonium salt, such as 1, 2, and 4-tricarboxylic acid and those sodium, and potassium salt, etc. are mentioned.

[0021] As partial saturation tetracarboxylic acid and those salts, it is 1-pentene. - They are 1, 1, 4, and 4-tetracarboxylic acid and 4-pentene. - They are 1, 2, 3, 4-tetracarboxylic acid, and 3-hexene. - Alkali-metal salts or ammonium salt, such as 1, 1, 6, and 6-tetracarboxylic acid and those sodium, and potassium salt, etc. are mentioned.

[0022] As a partial saturation sulfonic acid, alkali-metal salts or ammonium salt, such as a vinyl sulfonic acid, a styrene sulfonic acid, an allyl compound sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid and those sodium, and potassium salt, etc. are mentioned.

[0023] As partial saturation phosphonic acid, alkali-metal salts or ammonium salt, such as vinyl phosphonic acid, alpha-phenyl vinyl phosphonic acid and those sodium, and potassium salt, etc. are mentioned.

[0024] An itaconic acid, an acrylic acid, and its salts are desirable among the above-mentioned anionic vinyl monomers, and an itaconic acid and its salts are desirable especially. The approach of introducing an anion radical can also be used by hydrolyzing acrylamide system resin [B] with an acid or alkali in addition to the approach using an anionic vinyl monomer as the introductory approach of an anionic radical.

[0025] The Nonion nature vinyl monomer of the amount of extent which does not injure the compatibility of the cationic vinyl monomer of dimethylaminopropyl (meta) acrylamide, the 4th

class ghost of its, etc. which can be copolymerized, or the obtained resin constituent, and water solubility other than the above (a), (b), and the (c) component can also be used.

[0026] As a cationic vinyl monomer, for example Dimethylaminoethyl (meta) acrylate, Diethylaminoethyl (meta) acrylate, dimethylaminopropyl (meta) acrylate, Diethylamino propyl (meta) acrylate, dimethylaminopropyl (meta) acrylamide, or diethylamino propyl (meta) acrylamide, Salts of inorganic acids, such as vinyl monomers which have the 3rd class amino groups, such as an alkyl diaryl amine, dialkyl allylamine, a diaryl amine, and allylamine, the 2nd class amino group, and the 1st class amino group or those salts, a sulfuric acid, a formic acid, and an acetic acid, or an organic acid, [0027] Or alkyl halide, such as this the 3rd class amino-group content vinyl monomer, methyl chloride, and a methyl bromide, Aryl AKIRU halide, such as benzyl chloride and a benzyl star's picture, A dimethyl sulfate, a diethyl sulfate, epichlorohydrin, 3-chloro-2-hydroxypropyl trimethylammoniumchloride, The vinyl monomer containing the quarternary ammonium salt obtained by the reaction with the 4th class-sized agents, such as glycidyl trialkyl ammonium chloride, For example, 2-hydroxy - N, N, N, N', N'-pentamethyl-N'-[3-[(1-oxo--2-propenyl) amino] propyl]-1, and 3-pro pansy aminium dichloride etc. is illustrated. It is independent in these kinds, or two or more sorts can be used together and used.

[0028] As an Nonion nature vinyl monomer, acrylonitrile, meta-acrylonitrile, styrene, the methyl vinyl ether, the alkyl ester of an acrylic acid (meta), 2-hydroxy ester, or glycidyl ester is illustrated, it is independent in these kinds, or two or more sorts can be used together and used.

[0029] As a cross linking agent of the (d) component used for acrylamide system resin [B] Ethylene GURIKORUJI (meta) acrylate, diethylene GURIKORUJI (meta) acrylate, Di(meth) acrylate, such as TORIECHIRENGURIKORUJI (meta) acrylate and propylene GURIKORUJI (meta) acrylate GURISERINJI (meta) acrylate, a trimethylol propane ethyleneoxide addition product thoria chestnut rate, Methylenebis (meta) acrylamide, ethylene screw (meta) acrylamide, Screw (meta) acrylamides, such as - bis-acrylamide acetic-acid, and N'N, N'-bis-acrylamide methyl-acetate, N, and N-benzylidene bis-acrylamide, [hexa methylenebis (meta) acrylamide N, and] [0030] Divinyl ester, such as an adipic-acid divinyl and a sebacic-acid divinyl Epoxy acrylate, urethane acrylate, allyl compound (meta) acrylate, Diallyl phthalate, diallyl maleate, diaryl succinate, diaryl acrylamide, Divinylbenzene, diisopropylbenzene, N, and N-diaryl methacrylamide,

2 functionality vinyl monomers, such as diaryl dimethylannmonium, diallyl chlorendate, and glycidyl (meta) acrylate, 3 functionality vinyl monomers, such as 1, 3, 5-thoria chestnut roil hexahydro-S-triazine, triallyl isocyanurate, N, and N-diaryl acrylamide, a triaryl amine, and triallyl trimellitate, [0031] Tetramethylolmethane tetraacrylate, tetra-allyl compound pyromellitate, N, N, N', and N' - tetra-allyl compound-1,4-diaminobutane and a tetra-allylamine salt -- 4

functionality vinyl monomers, such as tetra-allyloxy ethane, tetramethylolmethane-tree beta-aziridinyl propionate, Trimethylol propane-tree beta-AJIRIJINIRUPUROPIONETO, Water-soluble aziridinyl compounds, such as 4 and 4'-screw (ethyleneimine carbonylamino) diphenylmethane, (Pori) Water-soluble polyfunctional epoxy compounds, such as ethylene glycol diglycidyl ether, propylene glycol (Pori) diglycidyl ether, glycerol (Pori) diglycidyl ether, and glycerol triglycidyl ether (Pori), [0032] And 3-(meta) acryloxy methyl trimethoxysilane, 3-(meta) acryloxypropyl dimethoxymethylsilane, 3-(meta) acryloxypropyltrimethoxysilane, 3-(meta) acryloxy propylmethyl dichlorosilane, 3-(meta) acryloxy octadecyl triacetoxysilane, 3-(meta) acryloxy -2,

5-dimethyl hexyl diacetoxymethylsilane, 3-(meta) acrylamide propyltrimethoxysilane, 2-(meta) acrylamide ethyl trimethoxysilane, 1-(meta) acrylamide methyl trimethoxysilane, 2-(meta) acrylamide-2-methylpropyl trimethoxysilane, 2-(meta) acrylamide-2-methylethyl trimethoxysilane, [0033] 2-(meta) acrylamide isopropyl trimethoxy silane, 3-(meta) acrylamide propyl triethoxysilane, N-(2-(meta) acrylamide ethyl) aminopropyl trimethoxysilane, Oxy-propyltrimethoxysilane, (3-(meta) acrylamide propyl) 3-(N-methyl (meta) acrylamide) propyltrimethoxysilane, 3-(meta) (acrylamide-methoxy)-3-hydroxypropyl trimethoxysilane, 3-(meta) (acrylamide-methoxy) propyltrimethoxysilane, 3-(vinylbenzyl aminopropyl) trimethoxysilane, [0034] Dimethyl-3-(meta) acrylamide-propyl -3 -(trimethoxysilyl)- Propyl ammoniumchloride, Dimethyl-2-(meta) acrylamide-2-methylpropyl -3 -(trimethoxysilyl)- Propyl ammoniumchloride, 3-(meta) acrylamide propylmethyl dimethoxysilane, 3-(meta) acrylamide propyl dimethyl METOKISHISHIRAN, 3-(meta) acrylamide propyl isobutyl dimethoxysilane, 2-

(meta) acrylamide propyl isobutyl dimethoxysilane, 2-(meta) acrylamide-2-methyl propyl monochloro dimethoxysilane, 2-(meta) acrylamide-2-methylpropyl hydrogen dimethoxysilane, [0035] 3-(meta) acrylamide propylbenzyl diethoxysilane, 3-(meta) acrylamide propyl triacetoxysilane, 2-(meta) acrylamide ethyl triacetoxysilane, 4-(meta) acrylamide butyl triacetoxysilane, 2-(meta)acrylamide-2-methylpropyltriacetoxysilane, N-(2-(meta) acrylamide ethyl) aminopropyl triacetoxysilane, 2-(N-ethyl (meta) acrylamide) ethyl triacetoxysilane, 3-(meta) acrylamide propyl OKUCHIRUJI acetoxysilane, 1-(meta) acrylamide methylphenyl diacetoxysilane, [0036] 3-(meta) acrylamide propyltripropionyloxy silane, 3-(meta) acrylamide pro PIRUTORI (N-methylaminoethoxy) silane, Vinyl trichlorosilane, vinyl methyl dichlorosilane, divinyl dichlorosilane, Vinyl phenyl dichlorosilane, vinyl dimethyl chlorosilane, vinyl methylphenyl chlorosilane, Vinyl diphenyl chlorosilane, vinyltrimetoxysilane, vinyl methyl dimethoxysilane, Vinyl isobutyl dimethoxysilane, a vinyl dimethyl methoxy silane, vinyltriethoxysilane, 3-vinylbenzyl aminopropyl triethoxysilane, vinyl methyldiethoxysilane, [0037] Divinyl diethoxysilane, a vinyl dimethylethoxy silane, a vinyl diphenyl ethoxy silane, A vinyl triisopropoxy silane, BINIRUTORI butoxysilane, vinyl dimethyl iso butoxysilane, Vinyl triphenoxysilane, a vinyl dimethyl (3-amino phenoxy) silane, A vinyl dimethyl (4-amino phenoxy) silane, a vinyl dimethyl (3-methyl-4-chloro phenoxy) silane, Silicon system compounds, such as a vinyl dimethyl (2-methyl-4-chloro phenoxy) silane, vinyltriacetoxysilane, a vinyl methyl diacetoxysilane, and vinyl dimethyl acetoxysilane, can be illustrated.

[0038] the front face of this invention -- quality of paper -- improvement liquids and solutions can be obtained by mixing resin [A] and acrylamide system resin [B] with a conventional method. The amount of the resin [A] used has desirable 1 - 50 weight section to the (Acrylamide b) 100 weight section used for acrylamide system resin [B], and especially its 3 - 30 weight section is desirable. The weight ratio of each component (a), (c), and (d) used for the reaction of the acrylamide system resin [B] of this invention As opposed to the (Acrylamide b) 100 weight section ureas (a) The 5 - 100 section, The ten to 60 section, it is the ten to 30 section still more preferably, and an anionic vinyl monomer (c) is the 2 - 20 section preferably the 0.5 to 50 section, and a cross linking agent (d) is the 0.01 - 2 section preferably the 0.005 to 10 section.

[0039] When the weight ratio of resin [A], ureas (a), and an anionic vinyl monomer (c) is except this range, surface reinforcement, internal reinforcement, and a size effect cannot be raised with sufficient balance, and it is not desirable. Moreover, when the weight ratio of a cross linking agent (d) exceeds this range, product viscosity is high and is not desirable.

[0040] Composition of the acrylamide system resin [B] used by this invention can be conventionally performed by various well-known approaches. For example, in a predetermined reaction container, two to 40% of the weight, monomer concentration can prepare each component and water so that it may become 5 - 30% of the weight preferably, it can add a polymerization initiator, and can obtain the acrylamide system resin [B] which is 40-100 degrees C in temperature under stirring, and is made into the purpose by performing the reaction of 0.5 - 10 hours. Of course, acrylamides (b), an anionic vinyl monomer (c), and a cross linking agent (d) component can also perform continuation dropping etc. according to the description of the component to be used.

[0041] Especially the polymerization initiator used for composition of the acrylamide system resin [B] of this invention is not limited, and the thing of well-known common use can be used for it. For example, radical polymerization initiators, such as sodium persulfate, potassium persulfate, ammonium persulfate, a hydrogen peroxide, and the second cerium salt, are used 0.01 to 5% of the weight to the sum total weight of acrylamides (b) and an anionic vinyl monomer (c). Moreover, the redox polymerization of the reducing agents, such as dimethylamine, a sodium hydrogensulfite, and sodium formaldehyde sulfoxylate, can also be used together and carried out.

[0042] Moreover, the chain transfer agent of well-known common use may be used if needed. For example, allyl compounds, such as allyl alcohol and allylamine, mercaptoethanol, thioglycolic acid, its alkali-metal salt or ammonium salt, isopropyl alcohol, sodium hypophosphite, etc. are mentioned.

[0043] the front face of this invention -- quality of paper -- additives, such as a non-skid agent,

a release agent, a rust-proofer, antiseptics, a defoaming agent, a viscosity controlling agent, a color, a surface sizing compound, and water repellent, may be added to the coating liquid containing improvement liquids and solutions or this. moreover, nature, such as starch, polyvinyl alcohol, and a carboxymethyl cellulose, or concomitant use with synthetic macromolecule, and the front face of further others -- quality of paper -- concomitant use with an improver is not restricted, either. In addition, as for the solid content concentration of coating liquid, it is desirable to usually be carried out at 0.1 - 15%.

[0044] the front face of this invention -- quality of paper -- it is desirable to carry out the surface coating liquid containing improvement liquids and solutions by the approach of size press, a film press, a gate roll coater, a blade coating machine, or a calender in carrying out coating to paper or the paper board. Moreover, coating can also be carried out by the bar coating machine, the knife coating machine, an air knife coater, etc.

[0045] moreover, the front face of this invention -- quality of paper -- coating of the coating liquid containing improvement liquids and solutions can be carried out to acid paper or alkaline paper. As a class of acid paper or alkaline paper, various stencil paper, such as coat stencil paper, a newsprint, a liner, a coat ball, printing writing paper, a form form, a PPC form, inkjet printing paper, a hot printing form, and a thermal paper, is mentioned. Although also whenever [size / of stencil paper] is arbitrary, when carrying out coating using size press etc., it is desirable to use an internal sizing compound in order to adjust the liquid adsorption of stencil paper.

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EXAMPLE

[Example] Although an example and the example of a comparison are given and this invention is hereafter explained to a detail, this invention is not limited to the following example. In addition, the section and especially % mean weight section and weight %, as long as there is no notice.

[0047] The synthetic example 1 (composition of acrylamide system resin [B])

The water 328 section, the urea 20 section, the 50% acrylamide water-solution 200 section, the itaconic-acid 4 section, and the isopropyl alcohol 35 section were taught to the 1l. 4 opening flask which attached an agitator, a thermometer, a reflux cooling pipe, and nitrogen gas installation tubing, and the temperature up was carried out to 60 degrees C. Subsequently, the ammonium persulfate water-solution 3.3 section was added 5% under nitrogen gas installation, the temperature up was carried out to 80 degrees C, and it was made to react for 2 hours. The water 30 section was added to the acquired resultant, and the water soluble resin of the solid content of 20.6%, the viscosity of 5500cps, and pH7.2 was obtained. Let this be Resin m.

[0048] Except changing suitably a class and the amount used, such as the synthetic example 2 - 7 ureas (a), acrylamides (b), an anionic vinyl monomer (c), and a cross linking agent (d), as Table 1, it carried out like the synthetic example 1 and resin n-s was obtained.

[0049] The 124 sections and 20% aqueous ammonia solution of GSA2302 (styrene-acrylic acid resin) were mixed by solid content conversion, and the ten sections were mixed for example 1 resin m by solid content conversion. Let the obtained mixed water solution be Resin M.

[0050] The resin [A] and acrylamide system resin [B] which are shown in one to examples 2-6 and example of comparison 5 table 2 were mixed like the example 1, and resin N-R and resin w-z (example of a comparison) were obtained. Moreover, let the case of Resin m be the example 1 of a comparison.

[0051] Example 7 above-mentioned resin M-R, Resin m, and w-z (example of a comparison) were diluted with water, and the coating liquid whose solid content concentration is 3% was prepared. The No.3 bar coating machine was used for the non-coating newsprint (basis weight 45 [g/m²]), and one side coating of this coating liquid was carried out to it, and it was dried with the drum dryer (for 80 degrees C and 50 seconds). Gas conditioning was carried out after desiccation for 24 hours in 20 degrees C and the air conditioned room of 65% of relative humidity, and various evaluation trials were presented after that. A result is shown in Table 3. In addition, the example which carried out coating only of the water was indicated to Table 3.

[0052] In addition, the evaluation trial was performed by the following measuring methods.

Surface reinforcement: Dry pick ; RI printing testing-machine, and nip width-of-face ink [of 10mm]; FINE INK. (Dainippon Ink & Chemicals make)

The paper after ink T.V.=20 or 24 printings turned, the condition was observed with the naked eye, and five-step evaluation was performed by making 1 into **, having made 5 as A.

internal: on the strength -- SUKOTTO bond (kgf-cm); -- it measured on the bond strength of 5kg/cm², and the conditions for 30 seconds using the internal bond tester (Kumagaya Riki Kogyo K.K. make).

size whenever: -- drop test (second); -- J.TAPPI It carried out according to 33 (water 5microl).

[0053] Double-sided coating (whenever [part / for // and 100m coating solution temperature / in nip pressure 20 kg/cm and coating rate] 50 degrees C) of the coating liquid prepared like

example 8 example 7 was carried out to non-coating neutral paper of fine quality (basis weight 82 [g/m²]) with the size press equipment for a trial (Kumagaya Riki Kogyo K.K. make), and it dried with the drum dryer (for 80 degrees C and 50 seconds). Measurement of the surface reinforcement of each coated paper, internal reinforcement, and size nature was performed like the example 7 after desiccation. A result is shown in Table 4.

[0054]

[Table 1]

表 1 アクリルアミド系樹脂 [B] の合成

	尿素類 (a)	アクリル アミド類 (b)	アニオン性 ビニルモノマー (c)	架橋剤 (d)	その他の モノマー	固形分 (%)	粘度 (cps)	pH
合成例 1 樹脂m	尿素 20	AAm 100	IA 4	—		20.6	5500	7.2
2 n	尿素 20	AAm 100	ViP 3 IA 1	—		20.1	5400	7.6
3 o	尿素 10	AAm 100	AMPS 3	—	AN10	20.5	6200	7.6
4 p	尿素 30	AAm 90 MAAm 10	AA 10	—		20.2	5500	7.7
5 q	尿素 15 チオ尿素 5	AAm 100	IA 2	MBAAm 0.1		20.6	4900	7.2
6 r	尿素 20	AAm 100	—	—		20.3	5500	7.1
7 s	—	AAm 100	IA 4	—		20.1	5300	7.3

表中の略号は下記の通りである。なお、表中の各成分の単位は重量部である。

AAm: アクリルアミド、 MAAm: メタクリルアミド、 IA: イタコン酸、 ViP: ビニルホスホン酸、
AMPS: 2-アクリルアミド-2-メチルプロパンスルホン酸、 AA: アクリル酸、 AN: アクリロニトリル、
MBAAm: メチレンビスアクリルアミド、

[0055]

[Table 2]

表 2 実施例 1～6、比較例 1～5

	樹脂 [A]	重量部 (固形分換算)	アクリルアミド系樹脂 [B]	重量部 (固形分換算)
実施例 1 樹脂M	GSA2302	10	樹脂m	124
2 N	SMA3000	5	m	124
3 O	GSA2302	10	n	124
4 P	SMA2000	20	o	123
5 Q	イソバン10	20	p	140
6 R	GSA2303	10	q	122
比較例 1 樹脂m	—	—	m	124
2 w	GSA2302	10	r	120
3 x	GSA2302	10	s	104
4 y	SMA3000	60	m	124
5 z	ドデセニル無水コハク酸	10	m	124

表中の略号は下記の通りである。

GSA2302 : スチレン-アクリル酸樹脂
GSA2303 : スチレン-アクリル酸-アクリル酸エステル樹脂
SMA3000 : スチレン-マレイン酸樹脂
SMA2000 : スチレン-マレイン酸樹脂
イソバン10 : イソブチレン-マレイン酸樹脂

[0056]

[Table 3]

表 3 実施例 7

	樹脂	表面強度	内部強度 (kg/cm)	サイズ度 (秒)
		ドライビック	スコットボンド	ドロップテスト
本 発 明	M	5	2.51	81
	N	5	2.53	75
	O	4	2.41	80
	P	4	2.45	85
	Q	4	2.40	68
	R	5	2.51	83
比 較	m	5	2.54	22
	w	3	2.15	79
	x	3	2.19	77
	y	3	2.11	91
	z	2	2.03	35
	水	1	1.51	20

[0057]

[Table 4]

表 4 実施例 8

	樹脂	表面強度	内部強度 (kg/cm)	サイズ度 (秒)
		ドライビック	スコットボンド	ドロップテスト
本 発 明	M	5	3.14	87
	N	5	3.20	75
	O	4	3.01	88
	P	4	3.06	92
	Q	4	3.07	78
	R	5	3.15	85
比 較	m	5	3.16	8
	w	3	2.80	81
	x	3	2.85	87
	y	3	2.77	98
	z	2	2.63	33
	水	1	2.51	7

[Translation done.]